

The corrosion test of the materials for the product Hydrogen energy

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1. Introduction

Hydrogen which can be produced by a steam reforming, a hydrolysis of water via a thermochemical water splitting will be one of the promising major secondary energy sources in the near future. Hydrogen can be stored and transported for a long distance with a lower loss when compared to electricity.

Iodine Sulfur thermochemical water splitting process(IS process) can produce a large amount of hydrogen effectively without an emission of greenhouse gases such as carbon dioxide by using a high temperature nuclear energy as a heat source with an expected process thermal efficiency of 40~50%[1].

In order to establish a small scale IS process system, materials for each component in the IS process should be selected and qualified under environments where each component can be operated for a long time.

Considering that the IS process is operated under very severe environments of iodine and sulfuric acids at a wide temperature range from room temperature to 900°C, material corrosion must be an important issue for an accomplishment of a successful IS process. Especially, a corrosion resistant material applicable to highly concentrated sulfuric acid of a high temperature should be found. Therefore, the present work is focused on the corrosion behavior of some commercial materials and fabricated materials in boiling sulfuric acid

2. Experimental

Corrosion tests of various materials were performed in a boiling 50wt% sulfuric acid condition at 125°C and a 98wt% sulfuric acid condition at 320°C.

Materials were divided into Fe-Ni-Cr alloys, Fe-xSi alloys(x=6, 10, 13%), Ni base alloys, Ta, Au, Zr and SiC. Dimensions of the specimens were 20mm x 20mm x 1mm with a 5mm diameter circular hole to be held over the specimen holder.

Corrosion cell made of a pyrex glass flask with a capacity of 1L was used. The corrosion cell was heated on a hot plate to maintain a stable boiling condition. Evaporated sulfuric acid was liquidified in a reflux condenser to minimize the evaporation loss. The immersion period was defined as the time between the moment when a boiling begins and the moment when the heater is shut down.

The weight before and after the immersion test was measured by using an electronic balance of the Metler model AT261. Specimens were washed ultrasonically in acetone for 5 minutes before weighing them and then

dried. Corrosion rate was calculated by dividing the weight loss by both the specimen surface area and the immersion period. The surface morphologies of the corroded materials were examined by using SEM equipped with EDS(JSM6360).

3. Results and discussion

Table 1 shows the chemical compositions of the major alloying elements for the various materials used for the corrosion test.

Table 1. Chemical composition for the corrosion tested specimen.

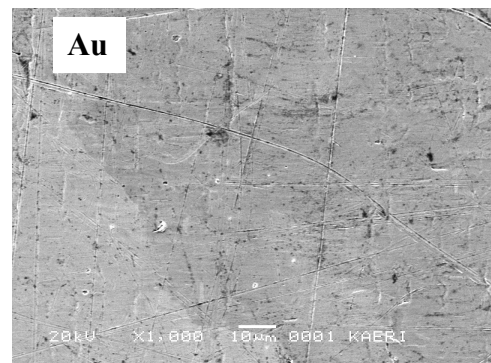
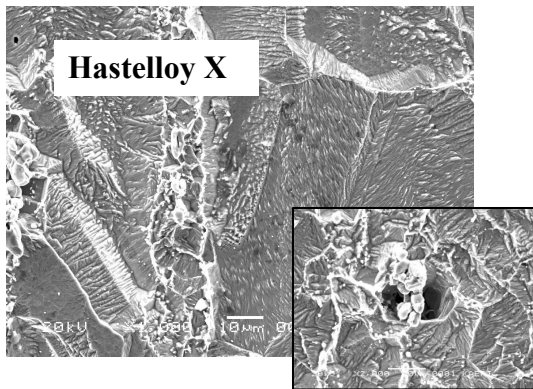
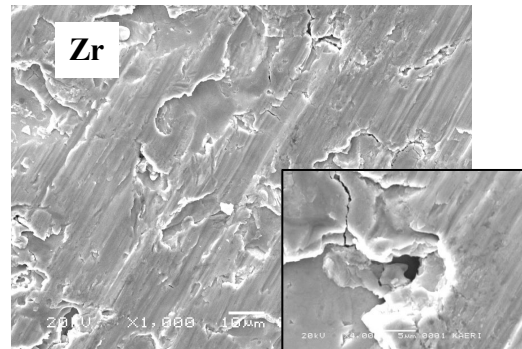
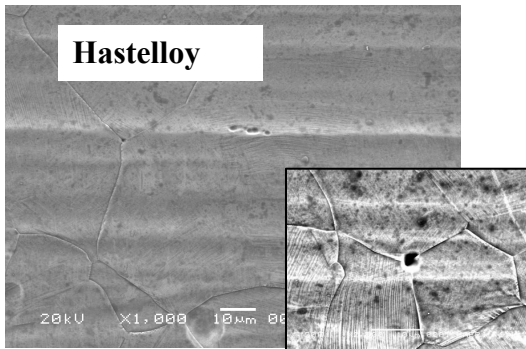
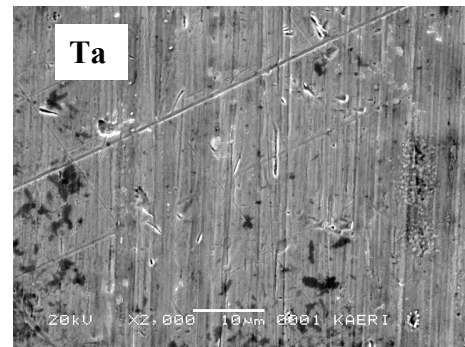
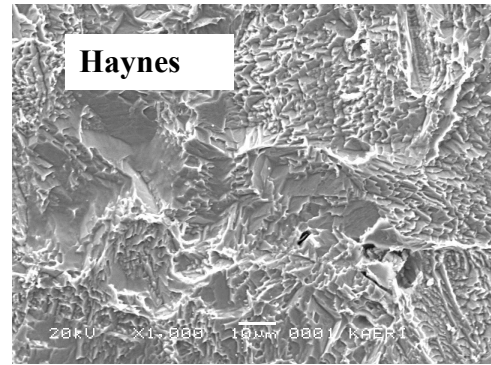
Specimen	Fe	Ni	Cr	Mo	Co	W
Alloy 690	7	Bal.	30			
Hastelloy C276	5	Bal.	15	15		3
Hastelloy X	18	Bal.	22	9	2	
Haynes 556	Bal.	20	22	3	18	2
Ta						
Zr						
Au						
SiC						
Fe-Si						

Table 2 shows the corrosion rates for the various materials tested in boiling 50wt% sulfuric acid. Alloy 690 was dissolved relatively severely indicating that the relatively high Cr content which provides most Fe-Cr alloys and Ni base alloys with a corrosion resistance was not affected. It seems that the corrosion resistance in 50wt% sulfuric acid is improved by alloying some Mo rather than Cr. Ta, Zr, Au and SiC showed an excellent corrosion resistance in the 50wt% sulfuric acid.

Fig. 1 illustrates the micrographs obtained from SEM for the specimens in 50wt% sulfuric acid. For Hastelloy C276, it seems that a general corrosion including a little grain boundary attack occurred and a pit was observed at a triple point where three grains were intersected. For Hastelloy X and Haynes 556, a similar appearance was observed, showing some spots like pits. On the other hand, surface appearances of Ta, Au and SiC were very clean indicating a corrosion resistance in boiling 50wt% H₂SO₄ at 125°C. It is notable that there was a pit on the surface of Zr in spite of its excellent corrosion resistance.

Table 2. Corrosion rate for various materials in boiling 50wt% sulfuric acid.

Specimen	Corrosion rate(mm/yr)
Alloy 690	194
Hastelloy C276	1.3
Hastelloy X	8
Haynes 556	9
Ta	0.003
Zr	0.02
Au	0.001
SiC	0.1



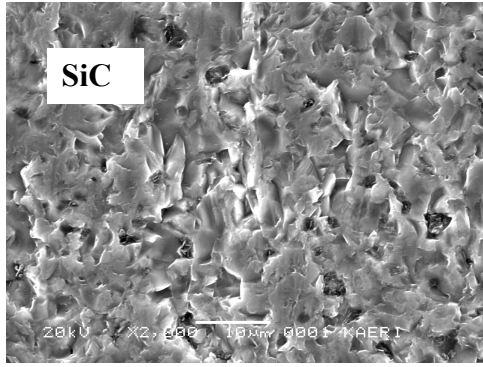


Fig. 1. Micrographs obtained from SEM for the specimens in 50wt% sulfuric acid.

Corrosion rates for various materials in boiling 98wt% sulfuric acid are presented in Table 3. When comparing the results in boiling 50wt% sulfuric acid, the tendency of a corrosion resistance in 98wt% sulfuric acid was different from the corrosion tendency in 50wt% sulfuric acid. In previous works [3,4] for the Fe-Cr alloys, the corrosion rate was increased with a decreasing Cr content. The high corrosion resistance of the Fe-Cr alloys in most corrosive environments is attributed to an enrichment of the Cr in the passive film on the Fe-Cr alloys [5].

Commercially pure Ni is highly resistant in many corrosive media, especially in reducing environments like a non-aerated solution of sulfuric acid where the surface of a passive Ni oxide film is usually stable. In many cases, the corrosion resistance of Ni can be improved by alloying it with Cu, Cr, Mo or W. In Cr-Ni alloys, the tendency to form a stable Cr₂O₃ surface film provides an appropriate stability for the Ni base alloys [6]. However, the Cr contents of Ni base alloys were not correlated with the corrosion resistance in this work. It seems that a certain amount of Mo is related to an improvement of the corrosion resistance in 98wt% sulfuric acid as well as in 50wt% sulfuric acid.

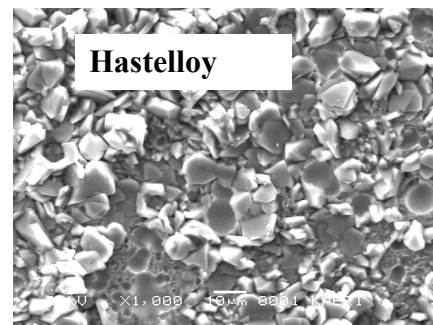
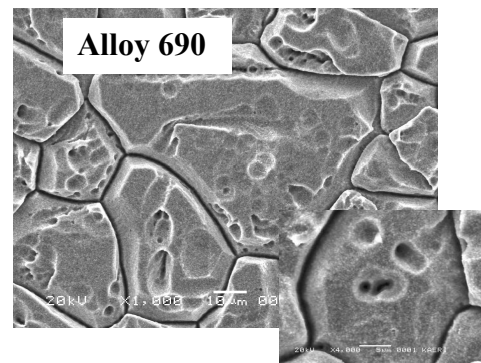
Au and SiC also showed an excellent corrosion resistance in 98wt% sulfuric acid while Ta showed a poor corrosion resistance.

Table 3. Corrosion rate for various materials in boiling 98wt% sulfuric acid.

Specimen	Corrosion rate(mm/yr)
Alloy 690	4
Hastelloy C276	1
Hastelloy X	0.4

Haynes 556	7
Ta	41
Au	0.04
SiC	0.1

Fig. 2 presents the micrographs obtained from SEM for the specimens in 98wt% sulfuric acid. For Alloy 690, severe grain boundary attack and numerous pits within the grains were observed, which were responsible for large corrosion rate of 4mm/yr. For Hastelloy C276, an oxide which was confirmed by using EDS(not shown here) was easily observed, which can be related to a passivation of Hastelloy C276 for 98wt% sulfuric acid. For Hastelloy X, an oxide was formed on the surface leading to an appropriate corrosion resistance. For Haynes 556, a general corrosion occurred. For Ta, a general corrosion was observed apart from an excellent corrosion resistance in 50wt% sulfuric acid. Oxides were observed on the surfaces of Au and SiC, which led to an excellent corrosion resistance in the 50 and 98wt% sulfuric acids.



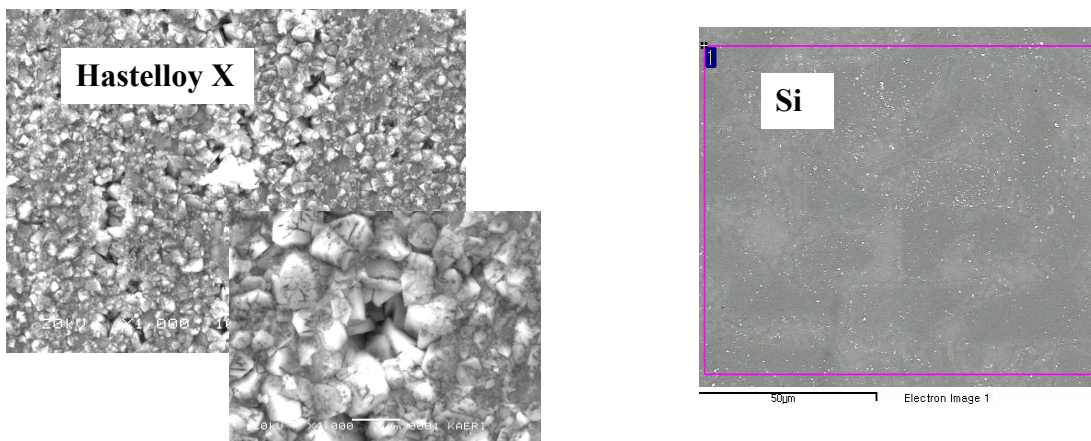
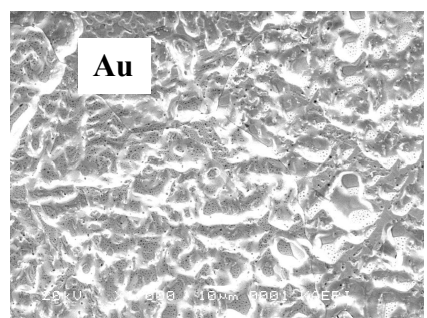
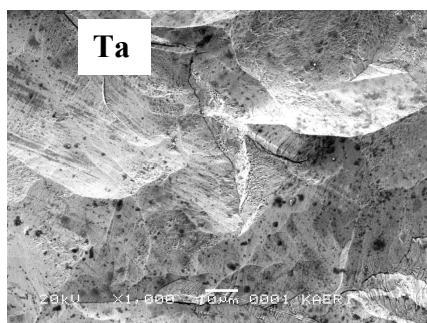
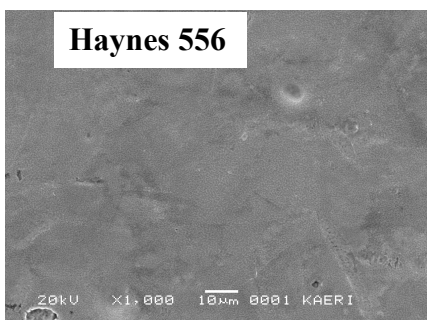


Fig. 2. Micrographs obtained from SEM for the specimens in 98wt% sulfuric acid.



With regards to Fe-xSi(x=6, 10, 13%), corrosion rates for Fe-6Si, Fe-10Si and Fe-13Si in boiling 98wt% sulfuric acid were about 1, 0.1 and 0.05mm/yr, respectively. According to previous works [3,4], corrosion resistance of Fe-Si was attributed to a Si enriched oxide.

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